Research paper

Formation of regular polyicosahedral structure during growth of large Lennard-Jones clusters from their global minimum

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ABSTRACT

Simulated growth of four global-minimum Lennard-Jones clusters of sizes N = 561, 823, 850 and 923, representing multishell icosahedra and decahedron, always leads to formation of regular polyicosahedral clusters. Observation of cluster structure evolution revealed that new atoms form anti-Mackay islands spreading over the cluster surface by making strong island-island junctions at cluster edges. Analysis of potential energies of atoms composing different local structures shows that energy-driven preference for decahedral arrangement of several atoms initiating the junction of pentagonal symmetry on the cluster surface is responsible for kinetic effect in the cluster growth.

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1. Introduction

There has been constant interest in theoretical analysis of structure of clusters because it determines their different properties such as phase stability during heating, external shape and growth mechanism. The main trend visible in the theory is to find a configuration of all N atoms in a cluster corresponding to the global minimum of cluster potential energy $E_p(N)$, which is called the global optimization method. When applied to a broad range of cluster sizes N, this method often reveals different structural types of global-minimum clusters even if they are modeled by the same interaction potential such as by the Lennard-Jones (LJ) potential for heavy rare-gas clusters. This is visible in very well investigated LJ clusters of $N \leqslant 309$, where several non-icosahedral morphologies are found besides the dominant icosahedral (ico) ones (see examples in Ref. [1]). In the case of larger LJ clusters of size in the range $561 \leqslant N \leqslant 923$, Shao et al. [2] and Xiang et al. [3] reported the structures of the global-minimum LJ clusters mainly in the icosahedral form created by addition of new atoms/particles to the Mackay icosahedron of N = 561. However, at some sizes it is observed that the global-minimum LJ clusters can have decahedral (dec) form [3] or an incomplete icosahedral form with empty core [2,3], i.e. without a central atom.

The weakness of the optimization method, based on finding the global minimum in potential energy E_p of an analysed cluster, lies mainly in neglecting the role of temperature. This is because minimization of the free energy $F = U - TS$, where the internal energy U is the sum of E_p and kinetic energy E_{kin} of a cluster, is necessary instead of only the potential energy E_p. Thus, the role of the cluster temperature T and the cluster entropy S in this method is neglected. Contribution of the entropic component "TS" to the free energy F is not negligible even for metallic clusters. For example, from the recent results of Sirenko and Belashchenko [4] it can be deduced that at room temperature it constitutes approximately 5%F for icosahedral silver cluster of N = 923. In the case of LJ clusters, Doye and Calvo [1] concluded the that role of entropy in determining its equilibrium structure is crucial. An additional unsolved problem in the global-minimum analysis of a cluster structure is the difficulty in explaining how completely different cluster structure could transform during a cluster growth. For example, transformation of icosahedral structure to decahedral one needs rebuilding of the entire cluster structure. Another problem is the omission of kinetic effects which can be important, if not decisive, in the structure formation of growing real clusters. As argued by Doye and Calvo [1], the role of temperature and entropy is very important in explaining structural transformations in clusters, while kinetic trapping could lead to non-equilibrium structures.

In this work, the ability of growth of the global-minimum structures is proved for LJ interaction. To reveal any kinetic processes in the case of ideal LJ cluster structures, growth simulations were done for four global minimum structures obtained by Xiang et al. [3] and available at the Cambridge Cluster Database [5]. The four selected clusters of different internal structure were used as nuclei

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in the existing two-temperature-region model [6] developed for atom-by-atom cluster growth based on Monte-Carlo (MC) simulations. The growth of a regular structure different from multishell icosahedral or decahedral clusters, commonly known to have the deepest minimum of potential energy for $N < 11,500$ [7], would be used as an argument for the important role of kinetic effects in the cluster growth.

2. Method

The Monte Carlo simulations of growth of the LJ clusters from the vapour were carried out at the reduced temperature $T^* = 0.35$ corresponding to 42 K for argon, which is very close to the range of experimental temperature of argon clusters 35 ± 4 K [8]. Four different clusters of size $N = 561$, 823, 850 and 923, obtained by Xiang et al. [3], were selected from the Cambridge Cluster Database [5] and used as seeds. The clusters have atomic configuration corresponding to the global minimum and represent the forms: Mackay icosahedra ($N = 561$ and 923), icosahedron with an empty atom position in the cluster centre ($N = 850$) [3], and Marks' decahedron ($N = 823$) [3].

After thermal equilibration of length 2×10^5 MC cycles, the clusters were grown using the two-temperature cluster growth model [6] in 15 independent simulation runs for every cluster size to attain the final size $N \approx 3300$. In the simulations, the classical LJ interaction potential $E_p(r_{ij}) = 4\varepsilon\left[(\sigma/r_{ij})^{12} - (\sigma/r_{ij})^6\right]$, where r_{ij} is the distance between i-th and j-th atom/particle in the system, was used; the potential was cut off at the distance $r_{cut} = 3.4\sigma$ without a shift. The values of the potential parameters σ and ε, characteristic for different rare gases, are used here as units of length and energy, respectively. The growth was realised by attachments to the nucleus/seed of single atoms when they contacted the cluster surface during their random movement in vapour region of atom concentration $n = 0.001\sigma^{-3}$ kept with 10% accuracy. This value of the concentration was proved to be low enough to enable the formation of well-ordered cluster structures [6,9]. The vapour temperature $T_v = 1.2\varepsilon/k_B$ ($T^*_v = 1.2$), where k_B is Boltzmann's constant, is high enough to avoid formation of small clusters in the vapour region. Moreover, fast diffusion of the vapour atoms to the growing nucleus is due to the large maximum displacement equal 0.7σ compared with 0.14σ for the nucleus atoms. The cubic simulation cell had the edge length $L = 35\sigma$, which is high enough in comparison with the final cluster diameter of 19σ. This means that the growing cluster occupies merely about 8% of the cell volume $V = L^3$. Therefore, the cluster was very well separated from its mirror images present due to the applied 3-dimensional periodic boundary conditions. Thus, a thick region of the surrounding vapour atoms assured uniform cluster growth in every direction.

Atoms of the growing cluster were detected in the simulated system using geometrical criterion with maximum atom-atom separation $r_{a-a} = 1.35\sigma$. This procedure was applied every 10-th MC cycle during simulations to actualise location of the cluster region with the lower temperature T extending up to r_{a-a} from the cluster atoms and surrounded by the vapour region of the temperature T_v. The clusters were subjected to structural analysis using the Coordination Polyhedron Method [10] and visualisation. This procedure enabled to reveal six types of local structure around the analysed atom: (i) crystalline structure represented by face-centred cubic (fcc), hexagonal close-packed (hcp) and bulk-centred cubic (bcc), (ii) non-crystalline structure of five-fold symmetry represented by icosahedral and decahedral structures, and (iii) disordered (dis) with a complete set of 12 neighbours but not forming any regular coordination polyhedron. To describe quantitatively an atom ordering in the cluster, value of the order

factor F_o (called also the cluster ordering parameter [10]) was obtained from the relation:

$$F_o = 1 - \frac{N_{dis}}{N_{12}}, \tag{1}$$

where N_{12} is the number of atoms surrounded by not less than 12 neighbours up to the distance $R_n = 1.4\sigma$ and N_{dis} is the number of the atoms among N_{12} which are centres of disordered (i.e. not-regular) units.

3. Results

The simulated thermal equilibration at $T^* = 0.35$ of the initial global-minimum clusters resulted in visible translations of some surface atoms, mainly from cluster vertices and edges as can be seen by comparing Fig. 1b and a. The translations lead to the occurrence of some atoms with disordered first shell near the cluster surface (Fig. 1c), though dominant part of the cluster atoms remains ordered preserving original directions of linear dec chains and location of the central ico unit (Fig. 1d). The anti-Mackay overlayer, reported by Doye and Wales [11] to occur in thermalized 561- and 923-atom Mackay icosahedra modeled by Morse potential, is not observed in any of the four equilibrated LJ clusters. The discrepancy can be attributed not only to different types of interatomic potentials, but mainly to low cluster temperature $T^* = 0.35$; a strong surface reconstruction, similar to that reported in Ref. [11], was observed during cluster heating at relatively high temperatures, for example at $T^* = 0.47$ for Mackay cluster LJ$_{923}$ [12].

Structural analysis of the final clusters of $N \approx 3300$ revealed that the simulations always lead to the formation of better or worse ordered regular polyicosahedral (r-PIC) clusters. Examples of such r-PIC clusters are shown in Fig. 2, where one can see that the close-to-spherical clusters have poor ordered surface (Fig. 2a) but atoms in the cluster interior are relatively well ordered with visible high symmetry of linear dec chains and the ico units located at crossing of these dec chains (Fig. 2b). The formed internal r-PIC structures can be described more precisely by adding the distance $d_{ico-ico}$, measured in interatomic distance r_0, between neighbouring ico units (or between crossings of the dec chains) as it was used in a recent paper [9]. For example, clusters B and D in Fig. 2b represent the r-PIC11 and r-PIC7 structures, respectively.

Two remaining clusters show dec chains only in a limited region of the cluster and of less regularity. Therefore, they can be called as defected polyicosahedral (d-PIC): d-PIC5 and d-PIC6, respectively for the clusters A and C. Atom ordering in clusters, as measured by the value of the F_o parameter defined by Eq. (1), decreases with the number of disordered atoms shown in Fig. 2c. Among the final clusters, clusters having larger value of the $d_{ico-ico}$ parameter, occurring especially for growth starting from the decahedron of $N = 823$, are better ordered.

The arguments for the formation of the d-PIC clusters are based on geometry. The growing r-PIC structure is based on the highly symmetric internal structure of global-minimum nucleus like multishell icosahedral clusters (MIC) of $N = 561$ or 923, characterised by the existence of 20 twinned fcc tetrahedrons. During the growth, it was observed that the newly formed cluster structure is always disturbed (see disordered atoms in clusters A, C and D in Fig. 2c) at large cluster sizes due to impossibility of filling the 3D space by the newly formed fcc tetrahedrons. This induces strain leading to lowering of the cluster ordering in the growing r-PIC clusters [9].

Structure types of all the final clusters, accompanied with averaged value of the cluster order parameter F_o and the binding energy $E_p(N)/N$ are collected in Table 1. Here one can see that the